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A Spectrophotometric Study of Equilibria Involving Mononuclear Chromium(VI) Species in Solutions of Various Acids[1]

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Reactions of $HCrO_4^-$ with H^+, Cl^-, HSO_4^-, NO_3^-, and OAc^- have been studied by following changes in the ultraviolet absorption spectrum. Mononuclear Cr(VI) species present in aqueous solutions of various common acids are found to be: a mixture of $HCrO_4^-$ and H_2CrO_4 in nitric and perchloric acids, $HCrO_4^-$ in acetic acid, CrO_3Cl^- in hydrochloric acid, and $CrSO_7^{2-}$ in sulfuric acid. Equilibrium constants for the reactions and spectra of the various Cr(VI) species are reported.

Acid solutions which are less than 4×10^{-4} *M* in chromium(VI) obey Beer's law between 230 and 350 mμ, indicating little or no interference from dimerization of $HCrO_4^-$ to form $Cr_2O_7^{2-}$, as is expected from published values of the equilibrium constant for dimerization.[2] The spectrum in solutions of pH between 2 and 4 in perchlorate media is due solely to $HCrO_4^-$. It has been found possible to study directly the equilibria

$$H^+ + HCrO_4^- \rightleftharpoons H_2CrO_4 \qquad (1)$$

$$HSO_4^- + HCrO_4^- \rightleftharpoons CrSO_7^{2-} + H_2O \qquad (2)$$

$$H^+ + Cl^- + HCrO_4^- \rightleftharpoons CrO_3Cl^- + H_2O \qquad (3)$$

by following changes in the absorption spectrum of $HCrO_4^-$ in the presence of the other reactants. The values of the equilibrium constants obtained are compared with those obtained previously for reactions of $HCrO_4^-$ with H_3PO_4 and $H_2PO_4^-$ [3] and with $HCrO_4^-$.[2]

Experimental

Reagent grade chemicals were used without further purification. Very pure water prepared by de-ionization of distilled water was used for all dilutions. Despite all precautions, solutions of Cr(VI) containing more than 1.0 *M* hydrogen ion slowly changed to Cr(III), probably through oxidation of water by Cr(VI). Therefore, studies made in solutions containing 3.0 *M* hydrogen ion were all performed on freshly prepared solutions which were discarded as soon as loss of Cr(VI) was detected. The determination of equilibrium constants for the reactions studied required accurate measurements of small changes in absorbance of various solutions. To minimize errors most studies were made at constant Cr(VI) concentration with varying concentrations of other reacting species at constant ionic strength maintained with sodium perchlorate.

In the study of reaction 1 the quantity $A - A_1$ was measured by direct comparison of acidified Cr(VI) solutions with one containing only $HCrO_4^-$. This operation required changing the slit width from 0.26 to 0.58 mm. Probably because 350 mμ is at the point of maximum absorbance on a very broad band this had no effect on the absorbance differences found with test solutions of differing $[HCrO_4^-]$. Dimerization of $HCrO_4^-$ to give $Cr_2O_7^{2-}$ was less than 10% of the total when no other reaction with $HCrO_4^-$ occurred and was negligible for all significant points.[3] Constant ionic strength was maintained using sodium perchlorate.

All measurements were made using 1.0-cm. quartz cells in a Beckman Model DU spectrophotometer with a cell compartment thermostated at 25.0 ± 0.5°.

Theoretical

Definitions of terms.

c = total concentration of Cr(VI) species in moles/liter
x = concentration of species reacting with $HCrO_4^-$
ϵ_1 = molar absorbance of $HCrO_4^-$
ϵ_2 = molar absorbance of reaction product containing Cr(VI)
$A_1 = \epsilon_1 c$
$A_2 = \epsilon_2 c$
A = absorbance of a particular solution
K_d = dissociation constant for a reaction product reacting with H_2O
K_f = formation constant for a reaction product $= 1/K_d$
μ = ionic strength

Given a fixed value for c, and $x \gg c$: For reactions 2 and 3 at constant (H^+) and constant ionic strength and for reaction 1 at constant ionic strength

$$K_d = (A - A_2)x/(A_1 - A) \qquad (4)$$

Rearranging

$$(x + K_d)/(A_1 - A_2) = x/(A_1 - A) \qquad (5)$$

Since, in all cases, species reacting with $HCrO_4^-$ are in high excess, A_1 and x are known for each solution while A can be measured. Thus, one can plot $x/(A_1 - A)$ *vs.* x, obtaining a straight line and intercept from which to calculate K_d (or K_f) and A_2.

Results

Figure 1 shows the effects of hydrogen ion, bisulfate ion, and chloride ion on the spectrum of $HCrO_4^-$. It was not possible to obtain solutions in which conversion of $HCrO_4^-$ to H_2CrO_4 was complete, since in concentrated perchloric acid reduction of Cr(VI) to Cr(III) by water was too rapid for quantitative observations on Cr(VI) to be made. Conversion of $HCrO_4^-$ to CrO_3Cl^- is essentially complete in 1.0 *M* hydrochloric acid. The spectrum of Cr(VI) remains essentially invariant between 1.0 and 8.0 *M* hydrochloric acid. In 9.0 to 12.0 *M* hydrochloric acid complicated, time-dependent changes in the ultraviolet spectrum occur. Conversion of $HCrO_4^-$ to $CrSO_7^{2-}$ is nearly complete in 1.0 *M* bisulfate solutions. The spectrum is varied only slightly in solutions ranging from 1.0 *M* sodium bisulfate to 3.0 *M* sulfuric acid. No evidence for reaction of $HCrO_4^-$ with nitrate ion or acetate ion could be observed. Thus it can be concluded that the mononuclear species of Cr(VI) present in dilute aqueous solutions of acids are: $HCrO_4^-$ in acetic acid, $HCrO_4^-$ and H_2CrO_4 in perchloric and nitric acids, $CrSO_7^{2-}$ in sulfuric acid, and CrO_3Cl^- in hydrochloric acid.

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(1) Presented before the Division of Inorganic Chemistry at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(2) J. Y. Tong and E. L. King, *J. Am. Chem. Soc.*, **75**, 6180 (1953).

(3) F. Halloway, *ibid.*, **74**, 225 (1952).

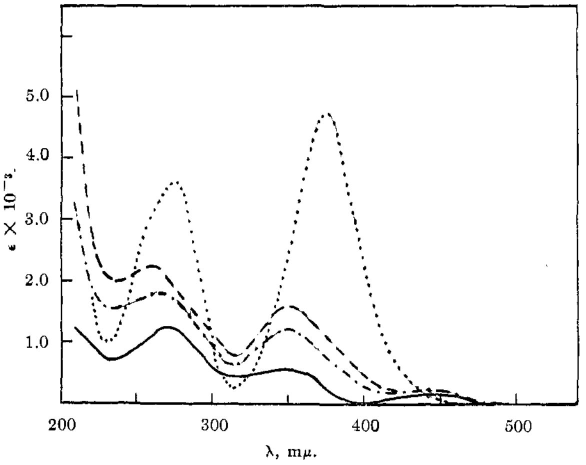

Fig. 1.—Absorption spectra of H_2CrO_4 ......, $HCrO_4^-$ – – – –, CrO_3Cl^- –·–·–·, and $CrSO_7^{2-}$ ———.

Equilibria. The Formation of Chromic Acid.—The nature of the data obtained upon adding perchloric acid to solutions containing $HCrO_4^-$ required that conclusions reached from the data be at best semiquantitative. Addition of perchloric acid to $HCrO_4^-$ decreases absorbance over the entire range from 220 to 400 mμ. There are in consequence no crossing points which could serve as tests for the presence of only two species. It has been assumed that the spectral changes are caused by formation of H_2CrO_4 and the data were analyzed accordingly. Figure 2 shows plots of eq. 5 for data obtained at 260 and 350 mμ at ionic strengths of 1.0 and 3.0, respectively. These wave lengths were selected because values of $A - A_1$ were greatest at these points. Table I gives results calculated from the plots of eq. 5 in Fig. 2.

Table I

Analysis of Plots in Figure 2[a]

Ionic strength	K_f (260 mμ)	K_f (350 mμ)	A_2 (350 mμ)	A_2 (260 mμ)
1.0	0.23	0.21	0.292	0.502
3.0	0.20	0.19	0.180[b]	0.352[b]

[a] A_1 (350 mμ) = 0.633; A_1 (260 mμ) = 0.852. [b] Preferred values.

Use of A_2 obtained from the plots for data at μ = 3.0 gives constant values for $K_f = 0.16$ when used with the data obtained at $\mu = 1.0$. On the other hand, K_f is not constant when calculated using A_2 obtained from the plot for $\mu = 1.0$ and the data obtained at μ = 3.0. Therefore we "prefer" the values for A_2 obtained at $\mu = 3.0$ which give $K_f = 0.16$ at $\mu = 1.0$ within the limits of experimental error. (It should be noted that if one assumes $A_2 = 0$ at any wave length from 220 to 350 mμ, the data give an excellent fit for the assumption that there is equilibrium between $HCrO_4^-$ and H_2CrO_4. The constants differ at most by a factor of three at the different wave lengths.) The plots in Fig. 2 give good agreement on values of K obtained at 260 and 350 mμ, indicating that such values are not far wrong. The "preferred" K_f values given above are probably accurate to ±20% of the true values.

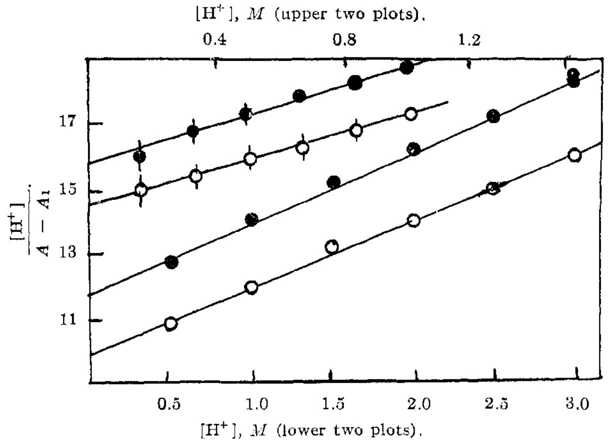

Fig. 2.—Plots of eq. 5 for the reaction of H^+ with $HCrO_4^-$. Lower two curves are for data at ionic strength = 3.0. Data at 350 mμ (solid dots) give $A_2 = 0.180$, $K_f = 0.19$, $A_1 = 0.633$. Data at 260 mμ (open circles) give $A_2 = 0.352$, $K_f = 2.0$, $A_1 = 0.852$. Upper two curves are for data at ionic strength = 1.0 and are displaced two units upward. Vertical lines indicate limits of error in measurement of experimental points. Data at 350 mμ (solid dots) give $A_2 = 292$, $K_f = 0.21$, $A_1 = 0.633$. Data at 260 mμ (open circles) give $A_2 = 0.502$, $K_f = 0.23$, $A_1 = 0.852$; (Cr(VI)) = 4×10^{-4} *M*.

Formation of $CrSO_7^{2-}$ from $HCrO_4^-$.—The addition of either H_2SO_4 or $NaHSO_4$ to solutions of $HCrO_4^-$ produces the same ultimate change in spectrum. Since 3.0 *M* $NaHSO_4$ and 3.0 *M* H_2SO_4 solutions of Cr(VI) show identical ultraviolet absorption spectra, it appears certain that $CrSO_7^{2-}$ is the only product of condensation of HSO_4^- with $HCrO_4^-$ and that no protonation of $CrSO_7^{2-}$ occurs at $[H^+] \leq 3.0$ *M*. Isosbestic points found in absorption spectra of Cr(VI) in varying concentrations of HSO_4^- support this conclusion. Meyer and Stateczny[4] have reported preparation of Na^+, K^+, and NH_4^+ salts of $CrSO_7^{2-}$ and the free acid by reactions carried out in the absence of water. Yatsimirski and Vasil'eva,[5] working at concentrations of Cr(VI) where polymerization of $HCrO_4^-$ is dominant, have found thermal and spectrophotometric evidence for several condensation copolymers of H_2CrO_4 and H_2SO_4. Figure 3 shows plots of eq. 5 for data obtained at 350 and 230 mμ, where x = (HSO_4^-). At 230 mμ the absorption curve for $CrSO_7^{2-}$ has a very steep slope whereas 350 mμ is an absorption maximum for both species. Therefore, values of $A_1 - A$ obtained at 350 mμ are more reliable. The equilibrium constant for the reaction $HSO_4^- + HCrO_4^- \rightleftharpoons CrSO_7^{2-}$ is found to be 4.1 ± 0.3 at ionic strength = 3.0 and 25°. All solutions used in this study had the same absorbance from 15 to 35°.

Formation of CrO_3Cl^- from $HCrO_4^-$ and H_2CrO_4.—For solutions in which ionic strength = $[H^+]$ = 1.0, Cr(VI) = 4×10^{-4} *M*, a family of ultraviolet absorption curves at various concentrations of chloride ion shows several isosbestic points. However, if $[Cl^-]$ = 1.0 *M*, isosbestic points are not observed as the hy-

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[4] J. Meyer and V. Stateczny, *Z. anorg. allgem. Chem.*, **122**, 1 (1922).

[5] K. B. Yatsimirski and V. N. Vasil'eva, *Zh. Neorgan. Khim.*, **1**, 984, 1983 (1956).

drogen ion concentration is varied. This observation is consistent with the existence in solution of three species, $HCrO_4^-$, CrO_3Cl^-, and H_2CrO_4. At constant $[H^+]$ the ratio $[HCrO_4^-]/[H_2CrO_4]$ remains constant so that isosbestic points appear despite the presence of *three* species. Since limiting absorbances for CrO_3Cl^- and for $[H_2CrO_4$ plus $HCrO_4^-]$ were accessible in this case, absorbances of solutions containing all three species could be used to calculate a constant

$$K_{obsd} = \frac{[CrO_3Cl^-]}{[(HCrO_4^-) + (H_2CrO_4)][Cl^-]} = \frac{(A' - A)}{(A - A_2)(Cl^-)} \quad (6)$$

where A' is the absorbance if no CrO_3Cl^- is formed. (A' is given by a mixture of $HCrO_4^-$ and H_2CrO_4.) Equation 6 is similar to eq. 4 with $[Cl^-] = x$ and A' substituted for A_1.

Let

$$K_a = \frac{[CrO_3Cl^-]}{[H_2CrO_4][Cl^-]} \quad K_b = \frac{[CrO_3Cl^-]}{[HCrO_4^-][Cl^-][H^+]}$$

$$K_f = \frac{[H_2CrO_4]}{[H^+][HCrO_4^-]} = \frac{K_b}{K_a} = 0.16 \text{ at } \mu = 1.0$$

Then

$$1/K_{obsd} = 1/(K_a[H^+]) + 1/K_b \quad (7)$$

Results are found in Table II which show clearly the small changes in absorbance with which we are dealing.

TABLE II

EFFECT OF Cl^- ON Cr(VI) SPECTRUM

$\mu = 1.0$ *M*; Cr(VI) $= 4.3 \times 10^{-4}$ *M*; $[H^+] = 1$ *M*

(Cl^-), *M*	A_{350}	K_{obsd}	A_{260}	K_{obsd}	A_{320}	K_{obsd}	
0.0	0.625	...	0.848	...	0.317	...	(A')
1.0	0.484	...	0.709	...	0.182	...	(A_2)
0.024	0.584	16	0.806	14	0.285	13	
0.048	0.565	15	0.788	16	0.265	13	
0.104	0.544	13	0.768	13	0.242	12	
0.208	0.516	16	0.742	15	0.216	14	

$K_{obsd} = 14 \pm 2$, $K_a = 105 \pm 20$, $K_b = 17 \pm 2$. Similarly at $\mu = 0.5$, $[H^+] = 0.5$ *M*, the following values were found. $K_{obsd} = 6.5 \pm 1.5$, $K_a = 100 \pm 20$, $K_b = 15 \pm 3$. Quite obviously the method of determination of these equilibrium constants is too uncertain to ascertain the effect of changing ionic strength.

Preparation of Potassium Chlorochromate ($KCrO_3Cl$).—The formation constants for the chlorochromate ion coupled with the value of 98 for the dimerization constant of $HCrO_4^-$ found by King and Tong[2] lead to the conclusion that even very concentrated chromium(VI) solutions in >3.0 *M* hydrochloric acid contain chiefly CrO_3Cl^-. Preparation of chlorochromates directly from such solutions should be possible and preferable to procedures involving chromyl chloride as suggested in *Inorganic Syntheses*.[6] Very pure samples of potassium chlorochromate have been prepared as follows. Enough $K_2Cr_2O_7$ to make a 1 *M* Cr(VI) solution is dissolved in hot 6 *M* HCl. The solution is cooled in an ice bath and crystals of $KCrO_3Cl$ separate. The crystals are filtered using sintered glass and dried in a vacuum desiccator over KOH or simply air dried on the filter. *Anal.* Calcd. for $KCrO_3Cl$: Cl, 20.3. Found: Cl, 20.1, 20.2.

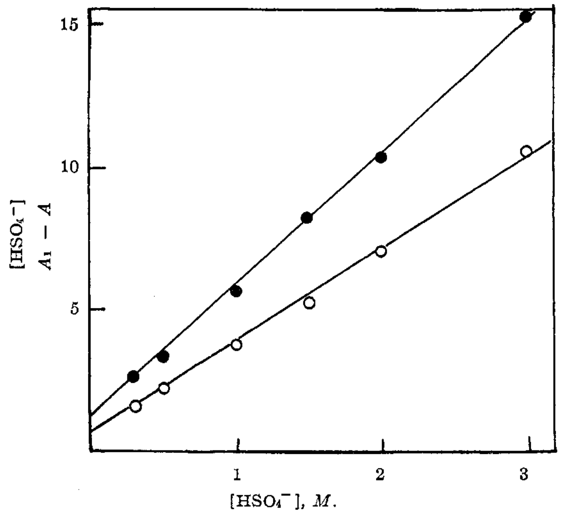

Fig. 3.—Plots of eq. 5 for the reaction of HSO_4^- with $HCrO_4^-$. Ionic strength = 3.0. Data at 350 mμ (solid dots) give $A_2 = 0.427$, $K_f = 3.9$, $A_1 = 0.642$. Data at 230 mμ give $A_2 = 1.455$, $K_f = 4.4$, $A_1 = 0.820$; $(Cr(VI)) = 4.06 \times 10^{-4}$ *M*.

Solutions of CrO_3 in 6 *M* HCl readily form precipitates with large alkylammonium ions, indicating CrO_3Cl^- salts may be generally prepared by this simple precipitation technique.

The Effect of Temperature Changes on Equilibria.—A_1 was found to be invariant with temperature over the range 10–35° and with ionic strength over the range 0.5–3.0 *M*. In the cases of $CrSO_7^{2-}$ and CrO_3Cl^-, A_2 was also found to be invariant with temperature. Thus temperature effects on absorbance are probably caused by shifts in equilibria in each case. The effect of temperature on absorbance of Cr(VI) solutions containing equilibrium mixtures of $HCrO_4^-$ and H_2CrO_4 is shown in Table III, while a similar study involving $HCrO_4^-$ and CrO_3Cl^- is shown in Table IV. ΔH and ΔS for the reactions were estimated from plots of log *K vs.* $1/T$. This change could be caused simply by the shift in the $HCrO_4^-$–H_2CrO_4 equilibrium with temperature, indicating the heat of formation of CrO_3Cl^- from $HCrO_4^-$ is nearly zero. No change in absorbance with temperature was observed for solutions containing $HCrO_4^-$ and $CrSO_7^{2-}$.

TABLE III

CHANGE OF ABSORBANCE OF 4×10^{-4} *M* (Cr(VI) IN 3 *M* $HClO_4$ WITH TEMPERATURE

T, °C.	A_{350}	A_{260}
17	0.467	0.682
19.5	0.462	
20.5		0.675
23.3	0.460	
25.0	0.458[a]	0.668[a]
27.0	0.457	0.665
32.0	0.450	0.657
ΔH,[b] kcal.	-1.8 ± 0.5	-2.4 ± 0.3
ΔS,[b] cal./deg.	3.0	2.2

[a] Rechecked after warming. [b] For $HCrO_4^- + H^+ \rightleftharpoons H_2CrO_4$.

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(6) H. H. Sisler, *Inorg. Syn.*, **2**, 208 (1946).

TABLE IV

CHANGE OF ABSORBANCE OF 4 × 10^{-4} M Cr(VI) in 0.1 M NaCl + 0.9 M $HClO_4$ WITH TEMPERATURE

T, °C.	A_{350}
10.2	0.521
18.0	0.517
22.0	0.511
25.8	0.510

Discussion

Table V compares various equilibria involving $HCrO_4^-$. The formation constants for chromic acid obtained in this study may be compared with the value of 1.2 obtained at ionic strength = 1.0 by King and Tong,[2] who measured the effect of changing hydrogen ion concentration on the dimerization of $HCrO_4^-$. The present authors feel that the value certainly lies between the values 4.5 and 6.5 on the basis of more direct means of measurement. It should also be noted that King and Tong[2] found it necessary to postulate the existence of $HCr_2O_7^-$ in order to fit their data, although they could find no change in absorbance due to its formation. If a value of about 5.0 for the dissociation constant of H_2CrO_4 is applied to the data of King and Tong the postulate that $Cr_2O_7^{2-}$ is protonated is no longer required.

TABLE V

THERMODYNAMICS OF $HCrO_4^-$ REACTIONS

	Ionic strength	K, l./mole	ΔF_{25}, kcal./mole	ΔH_{25}, kcal.	ΔS_{25}, cal./deg.
$HCrO_4^- + H^+ \rightarrow H_2CrO_4$	1.0	0.2[a] 0.83[b]	0.9 ± 0.2	−2.1	2.5
$HCrO_4^- + H^+ + Cl^- \rightarrow CrO_3Cl^- + H_2O$	1.0	17[a]	−1.7 ± 0.2	...	...
$HCrO_4^- + HSO_4^- \rightarrow CrSO_7^{2-} + H_2O$	3.0	4.1[a]	−0.85 ± 0.10	0.0	2.7
$HCrO_4^- + H_3PO_4 \rightarrow H_2CrPO_7^- + H_2O$	0.25	9.4[b]	−1.95	...	...
$HCrO_4^- + H_2PO_4^- \rightarrow HCrPO_7^{2-} + H_2O$	0.25	2.9[b]	−0.6	...	...
$HCrO_4^- + HCrO_4^- \rightarrow Cr_2O_7^{2-} + H_2O$	1.0	98[c]	−21.	...	...

[a] This work. [b] Ref. 3. [c] Ref. 2.

The results of the study of the formation of CrO_3Cl^- may be compared with those of Cohen and Westheimer,[7] who did the same study in 86.5% acetic acid. They found the same spectra of $HCrO_4^-$ and CrO_3Cl^- as those reported here and a formation constant (K_b) of 1.11 × 10^5. Acetic acid is a weakly ionizing medium and as such favors formation of CrO_3Cl^- much more than an aqueous medium.

Cohen and Westheimer[7] noted a similarity in the change in spectrum for Cr(VI) effected by substituting phosphate and chloride ions for hydroxide in the acid chromate ion. Substitution of sulfate can now be said to have about the same effect. It is notable that the ultraviolet absorption spectra of $HCrO_4^-$ and $Cr_2O_7^{2-}$ ions are nearly identical. Addition of protons to $HCrO_4^-$ to form chromic acid has quite a different effect on the spectrum from that of substitution for OH^- groups. The charge-transfer spectrum of CrO_4^{2-} exhibits small shifts in wave lengths for band maxima and considerable decrease in probability for electronic transitions upon the addition of one or two protons.

Acknowledgment.—The authors wish to thank the Office of Ordnance Research, United States Army, for the use of the Beckman Model DU spectrophotometer.

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[7] M. Cohen and F. H. Westheimer, *J. Am. Chem. Soc.*, **74**, 4389 (1952).

Notes

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Configurations of Isomeric Phenyl-N-dimethylaminotetraphosphonitriles. The Use of H^1 Nuclear Magnetic Resonance and Double Resonance Techniques

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In two recent papers[1,2] it was demonstrated that proton magnetic resonance spectra can be used to determine both positional and *cis–trans* configurations of a series of dimethylaminotriphosphonitriles. This paper extends the procedure to an analysis of the configurations of three phenyl-N-dimethylaminotetraphosphonitriles, $P_4N_4(C_6H_5)_4[N(CH_3)_2]_4$, and, by implication, substantially resolves the configurations of three phenylchlorotetraphosphonitriles, $P_4N_4(C_6H_5)_4Cl_4$, from which they were made. Specific configurations have not been reported previously for any of these compounds.

Cyclic tri- and tetraphosphonitriles of the formula $[NP(A)B]_3$ and $[NP(A)B]_4$ have the groups A and B attached to the phosphorus atoms. The bond angles are such that one group is above and the other is below the hypothetical plane of the ring and indicate the existence of geometric isomers. In the case of the trimer, two isomers can exist; for the tetramer, four

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[1] I. I. Bezman and C. T. Ford, *Chem. Ind.* (London), 163 (1963).

[2] C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, **3**, 177 (1964).